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The Role of Normally Hyperbolic Invariant Manifolds (NHIMs) in the Context of the Phase Space Setting for Chemical Reaction Dynamics

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Abstract

In this paper we give an introduction to the notion of a normally hyperbolic invariant manifold (NHIM) and its role in chemical rection dynamics. We do this by considering simple examples for one, two, and three degree-of-freedom systems where explict calculations can be carried out for all of the relevant geometrical stuctures and their properties can be explicitly understood. We specifically emphasise the notion of a NHIM as a "phase space concept". In particular, we make the observation that the (phase space) NHIM plays the role of "carrying" the (configuration space) properties of a saddle point of the potential energy surface into phase space.

We also consider an explicit example of a 2 degree-of-freedom system where a "global" dividing surface can be constructed using two index one saddles and one index two saddle. Such a dividing surface has arisen in several recent applications and, therefore, such a construction may be of wider interest.

1 Introduction

In recent years the phrase ''normally hyperbolic invariant manifold" (or NHIM) has made its way into the chemistry literature in relation to reaction dynamics. Probably the first use of the concept in the chemistry literature was in the Gillilan and Ezra study of a 3 degree-of-freedom van der Waals predissociation problem (Gillilan and Ezra (1991)) which used recently developed work of Wiggins (1990).

The notion of a NHIM is a standard concept and tool in dynamical systems theory. The theoretical framework was developed over the course of many years, beginning in the early part of the 20th century and reaching a mature form in the works of Fenichel (1971, 1974, 1977) and Hirsch *et al.* (1977). In Wiggins (1994) a (relatively) elementary exposition of Fenichel's approach to NHIMs is given with some discussion of applications. However, it is likely that a chemist seeking to learn about NHIMs from the mathematics literature will end up experiencing some level of frustration. While the mathematics associated with NHIMs is relatively new to the theoretical chemistry community, we believe that the results are no more difficult to understand or apply than various other fundamental concepts and results from nonlinear dynamics that are now well-established in theoretical chemical physics, e.g, the KAM theorem, invariant tori, stable and unstable manifolds, chaos, Arnold diffusion, cantori, turnstiles, separatrices, etc. The aim of this paper is to make this topic more accessible to theoretical chemists working in reaction dynamics by describing what a NHIM is, and its relevance to notions in reaction dynamics (most significantly, its role in the construction of dividing surfaces), in very simple settings where calculations can be carried out analytically, and their relation to physical quantities, such is kinetic, potential, and total energy can be understood and analyzed precisely. Most importantly, NHIMs are dynamical objects in phase space and therefore a detailed understanding of the geometry and dynamics in phase space in the context of reaction dynamics is essential. We will pay particular attention to contrasting phase space and configuration space concepts. See Waalkens and Wiggins (2010) for a related exposition, but from a more geometric point of view.

We first address the meaning of the phrase ''normally hyperbolic invariant manifold". In particular, we describe what each word signifies. For this, it is most instructive to start with the last word in the phrase and work backwards to the first.

Manifold. For our purposes, a manifold is just a surface. An isolated point is a trivial example of a surface.

Invariant. This means that the trajectory starting on the surface, remains on the surface ''forever" (i.e. infinitely into the future, and infinitely from the past).

Normally hyperbolic. Roughly speaking, this means that the invariant manifold has ''saddle-like" stability in directions ''transverse" to the manifold. More precisely, if we linearize the dynamical system about *any* trajectory on the invariant manifold we obtain a time varying *linear* system. The fundamental solution matrix of this system can be written as a linear combination of eigenvectors tangent to the invariant manifold and eigenvectors transverse to the manifold (eigenvectors of the fundamental solution matrix). Normal hyperbolicity means that the eigenvectors in the directions transverse to the manifold either grow or decay exponentially in time, and their rates of growth and decay are larger than any growth or decay of eigenvectors tangent to the manifold. For normal hyperbolicity of the manifold this property must hold *for every* trajectory in the manifold. We will see this explicitly in the examples below.

We will explicitly construct NHIMs, describe how NHIMs are used in the construction of phase space dividing surfaces (DSs), and describe the energy dependence of these objects in relation to index one saddle points on the potential energy surface (i.e. in configuration space). A significant feature of our discussion is that we carry out our construction for one, two, and three degrees-of-freedom (DoF). This highlights the fundamental difference between the geometrical structure of NHIMs in phase space as we go from one to two to three DoF. Indeed, the ''conceptual leap" that is probably most unfamiliar is the jump from two to three DoF, and we discuss this aspect in some detail.

We note that the theory of NHIMs does *not* depend on a Hamiltonian structure. Nevertheless, our discussion will be framed in the context of (continuous time) Hamiltonian systems since this is most relevant to the theory of chemical reaction dynamics. But before beginning our discussions of specific examples there are several overarching issues that we must discuss in the introduction in order to minimize ambiguities and confusion later on.

1.1 What do we mean by ''Reaction"?

It is important to explain what we mean by the term reaction in the context of the simple models described in this paper. In all of the models that we consider, one can think of the configuration space variables, i.e. $q_1, q_2, \ldots$, as describing bond lengths between atoms in a molecule. Reaction occurs when one (or more) bonds break. Mathematically this means that the particular coordinates defining the bonds become unbounded as they evolve in time.

For actual molecules, constructing mathematical models and identifying the coordinates that behave in this way, i.e. the *reaction coordinates*, is not so straight forward. Indeed, identifying the coordinates in a molecular model that describe the reaction is a substantial research area in chemistry. However, in all of our models there will be easily identifiable coordinates that can become unbounded (the saddle degrees-of-freedom, or saddle modes) with the remaining coordinates remaining bounded for all time (the bath modes). This will allow us to focus on NHIMs and other geometric structures in phase space and to determine their influence on reaction, as we have just described.

Another central issue is introduced in the following question.

1.2 Why do we work in phase space?

Given an initial state of a Hamiltonian system in order to *predict* the future motion we need the initial position *and* velocity. This is a basic property of differential equations, but we illustrate it with an example in a familiar context–the two well potential. In figure 1 a) we illustrate the two well potential energy. In figure 1 b) we illustrate the phase plane corresponding to the two well potential. In figure 1 c) we illustrate the configuration space of the two well Hamiltonian system. In figure 1 c) we denote a particular point in

the configuration space by the solid box and we ask the question of what is the future evolution of this point under Hamilton's equations? The answer is that the future evolution is not unique–it depends on the initial momentum. We illustrate this by showing the vertcal line in the phase plane located at the chosen point in configuration space. We see that it intersects many different curves in the phase plane. Each intersection corresponds to a different evolution of the solid box, depending on the value of the momentum intersected by the vertical line. Consideration of the phase space (as opposed to just the configuration space) makes it clear how the *momentum matters* in the future evolution of a given point in configuration space, and a consideration of the geometrical structures in phase space provides an understanding of the details of the dynamics. One might argue that widely accepted statistical models do not require direct use of the momentum (expect that the momentum does determine the kinetic energy). However, there is a growing appreciation of the importance and ubiquity of ''nonstatistical behavior" in chemical systems; see, e.g. Bunker and Hase (1973); Carpenter (1998, 2003a,b, 2005); Zheng *et al.* (2009); Glowacki *et al.* (2009); Goldman *et al.* (2011); Rehbein and Carpenter (2011).

For our purposes, practical aspects of this question are addressed in the next subsection.

1.3 Phase Space versus Configuration Space. The Hamiltonian versus the Potential Energy

NHIM's are ''phase space objects" (or ''dynamical objects"). They do not exist as a feature of the potential energy surface (PES). However, there is much effort in chemistry in attempting to understand dynamics from features of the PES. This often leads to some confusion with respect to the phase space point of view. Here we want to point out some of these issues in order to better clarify the role of NHIMs in dynamics.

We consider a n degree-of-freedom Hamiltonian of the following form:

$$H(q,p) = \sum_{i=1}^{n} \frac{p_i^2}{2} + V(q), \quad (q,p) \in \mathbb{R}^n \times \mathbb{R}^n, \tag{1}$$

where $q \in \mathbb{R}^n$ denote the configuration space variables and $p \in \mathbb{R}^n$ denote the corresponding conjugate momentum variables. This Hamiltonian function gives rise to the corresponding Hamilton's differential equations (or just ''Hamilton's equations") having the following form:

$$\begin{aligned} \dot{q}_i &= p_i, \\ \dot{p}_i &= -\frac{\partial V}{\partial q_i}(q), \quad i = 1 \ldots, n. \end{aligned} \tag{2}$$

These are a set of $2n$ first order differential equations defined on the phase space $\mathbb{R}^n \times \mathbb{R}^n$.

It will be important to keep in mind that there are three types of ''energy" represented in (1). The total energy, expressed as the Hamiltonian function $H(q.p)$, the kinetic energy, $\sum_{i=1}^{n} \frac{p_i^2}{2}$, and the potential energy, $V(q)$. We will take special care to describe exactly what type of energy we are discussing when the situation arises. If we only use the term ''energy" we will *always* mean total energy, the sum of the kinetic and potential energies.

1.3.1 The index of a saddle point

In analyzing differential equations, it is often easiest to start with the simplest dynamical objects–equilibrium points (a phase space concept). These can be directly related to critical points of the PES (a configuration space concept) in the way that we now describe.

Now a critical point of the potential energy function is a point $\bar{q} \in \mathbb{R}^n$ satisfying the following equations:

$$\frac{\partial V}{\partial q_i}(\bar{q}) = 0, \quad i = 1, \ldots n. \tag{3}$$

Once a critical point of the potential energy function is located, we want to ''classify" it. This is done by examining the second derivative of the potential energy function evaluated at the critical point. The second derivative matrix is referred to as the *Hessian matrix*, and it is given by:

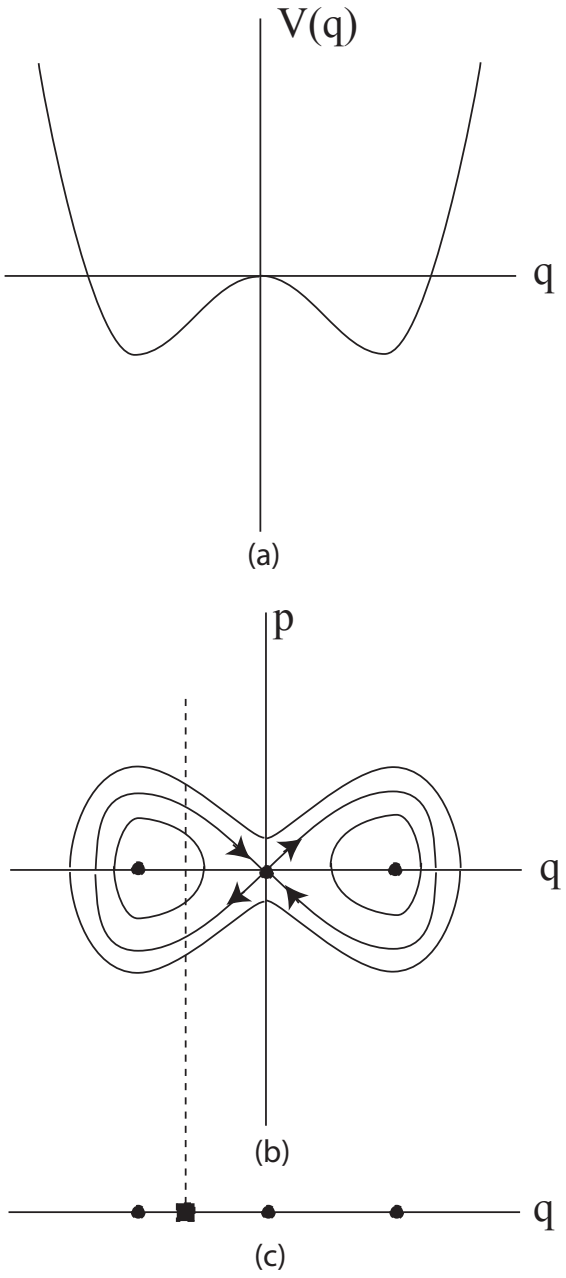

Figure 1: a) The two well potental energy. b) The phase space of the Hamiltonian system corresponding to the two well potential. c) The configuration space.

$$\frac{\partial^2 V}{\partial q_i \partial q_j}(\bar{q}) = 0, \quad i, j = 1, \ldots n, \tag{4}$$

which is a $n \times n$ symmetric matrix. Hence (4) has n real eigenvalues, which we denote by:

$$\sigma_k, \quad k = 1, \ldots, n. \tag{5}$$

However, returning to dynamics as given by Hamilton's equations (2), the point $(\bar{q}, 0)$ is an equilibrium point of Hamilton's equations, i.e. when this point is substituted into the right-hand-side of (2) we obtain $(\dot{q}_1, \ldots, \dot{q}_n, \dot{p}_1, \ldots, \dot{p}_n) = (0, \ldots, 0, 0, \ldots, 0)$, i.e. the point $(\bar{q}, 0)$ does not change in time.

Next, we want to determine the nature of the stability of this equilibrium point. Linearized stability is determined by computing the Jacobian of the right hand side of (2), which we will denote by M, evaluating it at the equilibrium point $(\bar{q}, 0)$, and determining its eigenvalues. The following calculation is from Ezra and Wiggins (2009b). The Jacobian of the Hamiltonian vector field (2) evaluated at $(\bar{q}, 0)$ is given by:

$$M = \begin{pmatrix} 0_{n\times n} & \mathrm{id}_{\mathrm{n\times n}} \\ -\frac{\partial^2 V}{\partial q_i \partial q_j}(\bar{q}) & 0_{n\times n} \end{pmatrix}, \tag{6}$$

which is a $2n \times 2n$ matrix. The eigenvalues of M, denoted by λ, are given by the solutions of the following characteristic equation:

$$\det\left(M - \lambda\, \mathrm{id}_{2n\times 2n}\right) = 0, \tag{7}$$

where $\mathrm{id}_{2n\times 2n}$ denoted the $2n \times 2n$ identity matrix. Writing (7) in detail (i.e. using the explicit expression for the Jacobian of (2)) gives:

$$\det \begin{pmatrix} -\lambda\, \mathrm{id}_{\mathrm{n\times n}} & \mathrm{id}_{\mathrm{n\times n}} \\ -\frac{\partial^2 V}{\partial q_i \partial q_j}(\bar{q}) & -\lambda \mathrm{id}_{\mathrm{n\times n}} \end{pmatrix} = \det\left(\lambda^2\, \mathrm{id}_{\mathrm{n\times n}} + \frac{\partial^2 \mathrm{V}}{\partial \mathrm{q_i} \partial \mathrm{q_j}}(\bar{\mathrm{q}})\right) = 0. \tag{8}$$

We can conclude from this calculation that the eigenvalues of the $n \times n$ symmetric matrix $\frac{\partial^2 V}{\partial q_i \partial q_j}(\bar{q})$ are $-\lambda^2$, where λ are the eigenvalues of the $n \times n$ matrix M. Hence, the eigenvalues of M occur in pairs, denoted by λ_k, λ_{k+n}, $k = 1, \ldots n$, which have the form:

$$\lambda_k,\, \lambda_{k+n} = \pm\sqrt{-\sigma_k}, \quad k = 1, \ldots, n, \tag{9}$$

where σ_k are the eigenvalues of the Hessian of the potential energy evaluated at the critical point $\bar{q}$ as denoted in (5). Hence, we see that the existence of equilibrium points of Hamilton's equations of ''saddle-like stability" implies that there must be *at least* one negative eigenvalue of (4). In fact, we have the following classification of the linearized stability of saddle-type equilibrium points of Hamilton's equations in terms of the critical points of the potential energy surface.

Index 1 saddle. One eigenvalue of (4) is positive, the rest are negative[1]. In the mathematics literature, these are often referred to as ''saddle-center-$\cdots$-center equilibria, with the number of center-$\cdots$-center terms equal to the number of pairs of pure imaginary eigenvalues.

Index 2 saddle. Two eigenvalues of (4) are positive, the rest are negative

and in general,

Index k saddle. k eigenvalues of (4) are positive, the rest are negative ($k \leq n$).

[1]We will assume that none of the eigenvalues of (4) are zero. Zero eigenvalues give rise to special cases that must be dealt with separately.

1.3.2 Dynamics on an Energy Surface and the ''Energy" of an Equilibrium Point of Hamilton's Equations

This is a very important point to clarify as it leads to some confusion in the literature and, we will see, it also is a key issue in understanding the importance of the NHIM.

For Hamilton's equations the Hamiltonian (or ''total energy") is a conserved quantity. To state this in an equivalent, but slightly different way, the level set of the Hamiltonian is a $2n-1$ dimensional invariant manifold denoted as:

$$\{(q,p) \in \mathbb{R}^n \times \mathbb{R}^n \,|\, T(p) + V(q) = H = \text{constant}\} \tag{10}$$

Now an equilibrium point of Hamilton's equations, $(q,p) = (\bar{q}, 0)$, has a fixed (total) energy:

$$0 + V(\bar{q}) \equiv H_e.$$

Then given a fixed (total) energy surface with (total) energy H, unless $H_e = H$, that equilibrium point cannot exist within that particular (total) energy surface. Therefore, we note the following important point that will be made clear in our examples:

> one role played by NHIMs is to carry the ''saddle point behavior", in a dynamical manner, to the energy surfaces above the energy of the equilibrium point of saddle type.

Finally, there is an ambiguity in terminology in the literature. The phrases "index k saddle", "rank k saddle", and "order k saddle" all refer to the same thing.

1.4 What is a dividing surface (DS)?

A geometrical object that is of great significance in chemical reaction dynamics is the notion of a *dividing surface* (DS). Mathematically, a dividing surface is simply a surface of one less dimension than the ambient space (i.e. it is said to have ''codimension one"), and having the property that trajectories pass through the DS.

While this particular definition is simple to state, there are several aspects that demand clarification. The first is ''what is the ambient space"? Thus far, we have considered three types of spaces–configuration space, phase space, and the energy surface (which is contained in phase space). In this paper we will be discussing and constructing DS in phase space. An associated important question is how do these DS vary as the energy is varied? We will revisit this question in Section 4. However, a significant amount of work in the chemistry literature considers DS in configuration space. This setting often obscures the dynamical aspects of a DS and its relationship to trajectories. This was discussed briefly in Section 1.2. More recently the desirability of a ''phase space dividing surface" has been noted in the chemistry literature in Shepler *et al.* (2008), and it is worth recalling that Wigner (1938) developed a fundamental cornerstone in chemical reaction dynamics theory–transition state theory, with a fully phase space formulation.

Another key question is ''what does the DS divide"? The answer to this question is in the spirit of the answer to the question ''what do we mean by reaction" discussed in Section 1.1, i.e., in our equations one (or more) configuration space coordinates became unbounded as time evolved (the mathematical manifestation of a bond breaking).

With respect to a DS, once we have a surface with the desired mathematical properties, e.g., codimension one in an energy surface, we need to ascertain the meaning of that surface in the context of the mathematical meaning of ''reaction" for our model equations. In particular, for that model, can it be viewed as a boundary between reactants and products? This is an additional criterion for a DS in a specific set of model equations that gives it ''chemical significance" for that model.

Once the characterization of the DS is established in this way, the rate at which trajectories cross this surface and, therefore, evolve from reactants to products can be related to the reaction rate. This also explains why the DS is constructed so that trajectories *cross* the DS.

1.5 How is a NHIM related to a dividing surface?

We will show in the examples that the NHIM, while *not* a DS, is the anchor for the construction of a DS having the "no-recrossing" property and the property of "minimal flux". In particular, the identification of a NHIM provides us with an algorithmic technique for constructing a DS having these properties.

1.6 Why do we desire a dividing surface with the ''no-recrossing" property?

The (directional) flux through the dividing surface is an important quantity used in the determination of a reaction rate. If the DS has the ''no-recrossing" property then the (directional) flux through the surface can be computed as an integral over the surface, i.e. there is no need to propagate trajectories in order to determine which trajectories initialized on the surface contribute to the directional flux). The ''no-recrossing" property is also the basis for the *minimal flux* property of DSs constructed from NHIMs, as discussed in Waalkens and Wiggins (2004)

This paper is organized as follows. Section 2 discusses, and constructs, NHIMs and DSs associated with index one saddles. The discussions and constructions are explicitly carried out for quadratic Hamiltonians (linear Hamiltonian vector fields for 1 DoF (Section 2.1), 2 DoF (Section 2.2) and 3 DoF (Section 2.3). In Section 2.4 we discuss the similariities and differences of the results for different numbers of DoF. In Section 3 we discuss an example of a ''global" dividing surface associated with index one *and* index two saddles. This is a situation that has arisen in several recent examples (Collins *et al.* (2012); Harding *et al.* (2012); Suits and Parker (2014)). In Section 4 we summarize our results and give an outlook for future research along these lines.

2 NHIMs and DSs in Phase Space Associated with Index One Saddles

In this section we will construct NHIMs and DSs associated with index one saddles. We will consider quadratic Hamiltonians having index one saddle points for one, two, and three DoF. The simplicity of these models will enable us to carry out exact calculations of the relevant geometrical objects and the understand their interrelations, energy dependencies and how these features change with dimension.

2.1 A One Degree-of-Freedom Saddle Equilibrium Point

The Hamiltonian for a linear one DoF saddle point is given by:

$$H = \frac{\lambda}{2}\left(p^2 - q^2\right), \quad \lambda > 0, \tag{11}$$

and the associated Hamilton's equations are:

$$\begin{aligned} \dot{q} &= \frac{\partial H}{\partial p} = \lambda p, \\ \dot{p} &= -\frac{\partial H}{\partial q} = \lambda q. \end{aligned} \tag{12}$$

In Fig. 2 a) we show a graph of the potential energy and in Fig. 2 b) we show the phase portrait corresponding to (11).

In this simple system ''reaction" corresponds to trajectories that change sign in q, which requires $H > 0$ (as shown in Fig. 2 b)). Non-reacting trajectories have $H < 0$.

Now we discuss the NHIM, its stable and unstable manifolds, and their role in constructing the DS. All of these notions are ''trivial" in this simple setting, but they will serve to focus the ideas when we consider more DoF.

For this case the NHIM is the saddle point at the origin (a single ''point" is a trivial example of a manifold). It only exists on the $H = 0$ energy surface (this is very different when we go to two, and more, DoF since in

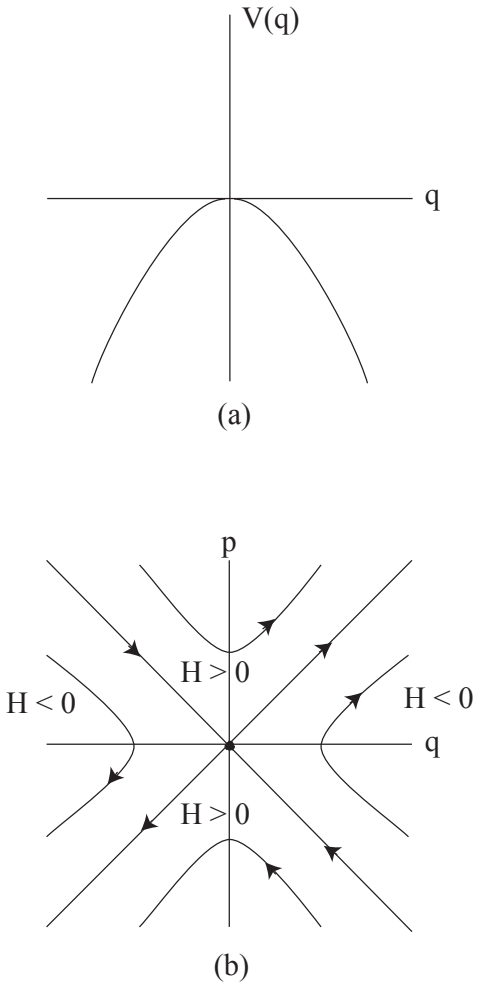

Figure 2: a) The potential energy, $V(q) = -\frac{\lambda}{2}q^2$, for a one DoF saddle. b)The phase space for the one DoF saddle.

these cases we will see that the NHIM can vary with energy) and its stable and unstable manifolds are the diagonal lines (also on the $H = 0$ energy surface–the stable and unstable manifolds of a NHIM have the same energy as the NHIM). A general feature of all NHIMs is that they have stable and unstable manifolds. The stable and unstable manifolds are *invariant* manifolds. That is, any trajectory that starts on one of these manifolds must remain on the manifolds throughout all of their past and future. The statements can be seen directly from the equations for the stable and unstable manifolds:

$$W^u\left((0,0)\right) = \{(q,p)\,|\,q = p\}\,, \tag{13}$$
$$W^s\left((0,0)\right) = \{(q,p)\,|q = -p\,\}\,. \tag{14}$$

It is easy to verify from (11) that each of these manifolds (''lines") is on the $H = 0$ energy surface–the same as the saddle point $(q,p) = (0,0)$. Since these manifolds are contours of the Hamiltonian they are clearly invariant manifolds. However, this can also be seen directly from the equations. We consider the unstable manifolds, $q = p$. If we substitute this constraint into (12) we see that the constraint is always preserved:

$$\begin{aligned} \dot{q} &= \lambda q, \\ \dot{p} &= \lambda p, \end{aligned} \tag{15}$$

and both $q(t)$ and $p(t)$ grow exponentially as $t \to \infty$. Similar reasoning can be applied to the stable manifold, $q = -p$ (except that $q(t)$ and $p(t)$ decay exponentially as $t \to \infty$).

A consequence of invariance, is that no trajectory can ''cross" these manifolds. Therefore stable and unstable manifolds of NHIMs act as ''barriers to transport in phase space". Moreover, we see from Fig. 2 b) that they form the boundary between reactive and non-reactive trajectories. These features of NHIMs and their stable and unstable manifolds in relation to reactive and non-reactive trajectories hold for more than one DoF, as we will show in later sections.

The non-isoenergetic DS can be taken as the vertical line $q = 0$. Clearly, it has the ''no-recrossing" properties and all reacting trajectories must cross this line. The DS at a fixed (positive) energy is given by

$$\frac{\lambda}{2} p^2 = H = \text{constant}, \tag{16}$$

or

$$p = \pm \sqrt{\frac{2}{\lambda} H}.$$

So for a fixed energy $H > 0$ the DS consists of two distinct *points*: $p = +\sqrt{\frac{2}{\lambda} H}$ (the dividing surface for forward reactions) and $p = -\sqrt{\frac{2}{\lambda} H}$ (the dividing surface for backward reactions). These points are just the intersection of the reacting trajectories with $q = 0$.

2.2 A Two Degree-of-Freedom Saddle-Center Equilibrium Point

The Hamiltonian for a linear 2 DoF system having an equilibrium point of saddle-center equilibrium type is given by:

$$H = \underbrace{\frac{\lambda}{2}\left(p_1^2 - q_1^2\right)}_{H_1} + \underbrace{\frac{\omega}{2}\left(p_2^2 + q_2^2\right)}_{H_2}, \quad \lambda, \omega > 0, \tag{17}$$

with the corresponding Hamilton's equations given by:

$$\begin{aligned} \dot{q}_1 &= \frac{\partial H}{\partial p_1} = \lambda p_1, \\ \dot{p}_1 &= -\frac{\partial H}{\partial q_1} = \lambda q_1, \\ \dot{q}_2 &= \frac{\partial H}{\partial p_2} = \omega p_2, \\ \dot{p}_2 &= -\frac{\partial H}{\partial q_2} = -\omega q_2, \end{aligned} \tag{18}$$

In Fig. 3 a) we show contours of the potential energy and in Fig. 2 b) we show the phase portrait corresponding to (17). Since the Hamiltonians H_1 and H_2 are uncoupled we can sketch the phase portraits for each separately. Also, H_1 corresponds to the ''reactive mode" and H_2 is a ''bath mode" and, in this decoupled case, we are able to discuss the distribution of total energy between each mode in a simple manner. We note that $(q_1, p_1, q_2, p_2) = (0, 0, 0, 0)$ is an index one saddle point for the full two DoF system on the zero (total) energy surface.

Recall that in our discussion of the 1 DoF saddle we considered the NHIM first, its stable and unstable manifolds second, and the DS last. For the 2 DoF index one saddle we will turn the order of discussion

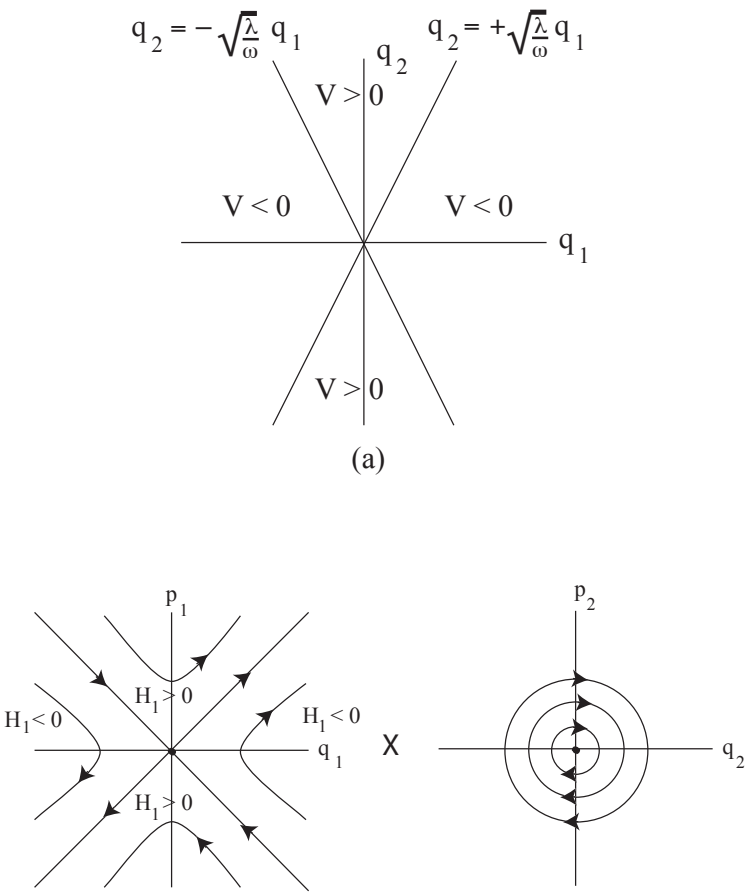

Figure 3: a) Contours of the potential energy, $V(q_1, q_2) = -\frac{\lambda}{2}q_1^2 + \frac{\omega}{2}q_2^2$, denoting the sign of $V(q_1, q_2) =$ constant. b) The phase space for the two DoF (index one) saddle defined by (18).

around by considering the DS *first*, the NHIM second, and the stable and unstable manifolds of the NHIM last. This will serve to highlight the fundamental role of the NHIM in the structure of the DS.

In this system reaction occurs when the q_1 coordinate of a trajectory changes sign. Hence, a ''natural" dividing surface would be $q_1 = 0$. This is a three dimensional surface in the four dimensional phase space. We want to examine its structure more closely and, in particular, its intersection with a fixed energy surface.

First, we need to discuss the energetics of reaction. For reaction to occur we must have $H_1 > 0$, since the q_1 component of reacting trajectories must change sign. Also, it is clear from the form of H_2 that $H_2 \geq 0$. Therefore, for reaction we must have $H = H_1 + H_2 > 0$.

The energy surface is given by:

$$\frac{\lambda}{2}\left(p_1^2 - q_1^2\right) + \frac{\omega}{2}\left(p_2^2 + q_2^2\right) = H_1 + H_2 = H > 0, \quad H_1 > 0,\, H_2 \geq 0. \tag{19}$$

The intersection of $q_1 = 0$ with this energy surface is given by:

$$\frac{\lambda}{2}\, p_1^2 + \frac{\omega}{2}\left(p_2^2 + q_2^2,\right) = H_1 + H_2 = H > 0, \quad H_1 > 0,\, H_2 \geq 0. \tag{20}$$

This is the isoenergetic DS. Its' equation has the form of a 2-sphere in the four dimensional (q_1, p_1, q_2, p_2) space. It has two ''halves" (''hemispheres") corresponding to DSs for the forward and backward reactions, respectively:

$$p_1 = +\sqrt{\frac{2}{\lambda}}\sqrt{H_1 + H_2 - \frac{\omega}{2}\left(p_2^2 + q_2^2\right)}, \quad \text{forward DS}, \tag{21}$$

$$p_1 = -\sqrt{\frac{2}{\lambda}}\sqrt{H_1 + H_2 - \frac{\omega}{2}\left(p_2^2 + q_2^2\right)}, \quad \text{backward DS}. \tag{22}$$

Since $\dot{q}_1 = \lambda p_1$, it is clear that the DS, being defined by $q_1 = 0$ is a surface having the ''no-recrossing" property.

The forward and backward DS ''meet" at $p_1 = 0$:

$$\frac{\omega}{2}\left(p_2^2 + q_2^2, \right) = H_1 + H_2 \geq 0, \quad \text{NHIM}, \tag{23}$$

which is an unstable periodic orbit in the $p_2 - q_2$ plane. The orbit is normally hyperbolic since it is of saddle-type stability. From (18), we see that the coordinates ''normal" to the periodic orbit are $q_1 - p_1$, and the dynamics in these coordinates is linear and of saddle type. This is the NHIM for this 2 DoF system. In this particular example, and in the case where the NHIM is one orbit, normal hyperbolicity is easy to understand since it is a characteristic of the linearized stability of that particular orbit.

Note that for $H_1 = 0$ and $H_2 = 0$ the NHIM reduces to the point $(q_1, p_1, q_2, p_2) = (0, 0, 0, 0)$, which is the index one saddle point for the full two DoF system on the energy surface $H_1 + H_2 = 0$. Hence, as the total energy is increased from 0, with H_2 increasing from zero, we see that the NHIM ''grows" from the index one saddle point on the zero energy surface. It is in this way, as noted in the introduction, that the ''influence" of the index one saddle point is carried to energies higher than the energy of the index one saddle point.

The stable and unstable manifolds of the NHIM are given by:

$$W^u\left(\text{NHIM}\right) = \left\{(q_1, p_1, q_2, p_2) \,|\, q_1 = p_1, \, \frac{\omega}{2}\left(p_2^2 + q_2^2\right) = H_2 > 0\right\}, \tag{24}$$

$$W^s\left(\text{NHIM}\right) = \left\{(q_1, p_1, q_2, p_2) \,|q_1 = -p_1, \, \frac{\omega}{2}\left(p_2^2 + q_2^2\right) = H_2 > 0\right\}. \tag{25}$$

These stable and unstable manifolds are each two dimensional on a fixed three dimensional energy surface. They have the structure of the cartesian product of a line ($q_1 = p_1$ or $q_1 = -p_1$) with a circle ($\frac{\omega}{2}\left(p_2^2 + q_2^2\right) = H_2 > 0$). Mathematically, this is a cylinder. The energy of these manifolds is determined as follows. The lines ($q_1 = p_1$ or $q_1 = -p_1$) correspond to the contour $H_1 = 0$. Therefore, in the four dimensional phase space, these manifolds have energy:

$$H = H_1 + H_2 = 0 + H_2 > 0.$$

Using the same argument as we gave for the 1 DoF saddle, we choose a point (q_1, p_1, q_2, p_2) on $W^u\left(\text{NHIM}\right)$. As $t \to \infty$ the (q_2, p_2) components evolve periodically and the (q_1, p_1) grow at an exponential rate as $t \to \infty$. Similarly, if we choose a point (q_1, p_1, q_2, p_2) on $W^s\left(\text{NHIM}\right)$. As $t \to \infty$ the (q_2, p_2) components evolve periodically and the (q_1, p_1) decay to zero at an exponential rate as $t \to \infty$. In other words, trajectories starting in $W^u\left(\text{NHIM}\right)$ decay at an exponential rate to the NHIM as $t \to -\infty$ and trajectories starting in $W^s\left(\text{NHIM}\right)$ decay at an exponential rate to the NHIM as $t \to \infty$.

Finally, we note that a detailed development of reaction dynamics for two DoF systems using periodic orbits was given in a beautiful series of papers by Pollak, Pechukas, and Child in the late 1970's to early 1980's (Pechukas and Pollak (1979); Pollak *et al.* (1980); Child and Pollak (1980). However, unstable periodic orbits and their stable and unstable manifolds did not have the proper dimensions to develop an analogous reaction rate picture systems with more than 2 DoF. The development of this story needed to wait until the introduction of the notion of a NHIM in its full (phase space and dimensional) generality, which we now describe.

2.3 The Three Degree-of-Freedom Saddle-Center-Center Equilibrium Point

The Hamiltonian for a (linear) 3 DoF system having an equilibrium point of saddle-center-center equilibrium type is given by:

$$H = \underbrace{\frac{\lambda}{2}\left(p_1^2 - q_1^2\right)}_{H_1} + \underbrace{\frac{\omega_2}{2}\left(p_2^2 + q_2^2\right)}_{H_2} + \underbrace{\frac{\omega_3}{2}\left(p_3^2 + q_3^2\right)}_{H_3}, \quad \lambda,\, \omega_2,\, \omega_3 > 0 \tag{26}$$

with the corresponding Hamilton's equations given by:

$$\begin{aligned}
\dot{q}_1 &= \frac{\partial H}{\partial p_1} = \lambda p_1, \\
\dot{p}_1 &= -\frac{\partial H}{\partial q_1} = \lambda q_1, \\
\dot{q}_2 &= \frac{\partial H}{\partial p_2} = \omega_2 p_2, \\
\dot{p}_2 &= -\frac{\partial H}{\partial q_2} = -\omega_2 q_2, \\
\dot{q}_3 &= \frac{\partial H}{\partial p_3} = \omega_3 p_3, \\
\dot{p}_3 &= -\frac{\partial H}{\partial q_3} = -\omega_3 q_3,
\end{aligned} \tag{27}$$

Since the Hamiltonians H_1, H_2 and H_3 are uncoupled we can analyze the phase portraits for each separately. As in the previous examples, H_1 corresponds to the ''reactive mode" and H_2 and H_3 are ''bath modes". We note that $(q_1, p_1, q_2, p_2, q_3, p_3) = (0, 0, 0, 0, 0, 0)$ is an index one saddle point for the full three DoF system on the zero (total) energy surface.

As in the previous examples, in this system reaction occurs when the q_1 coordinate of a trajectory changes sign. Hence, a ''natural" dividing surface would be $q_1 = 0$. This is a five dimensional surface in the six dimensional phase space. We want to examine it's structure more closely and, in particular, its intersection with a fixed energy surface.

First, note that for reaction to occur we must have $H_1 > 0$. Also, it is clear from the form of H_2 and H_3 that $H_2 \geq 0$ and $H_3 \geq 0$. Therefore, for reaction we must have $H = H_1 + H_2 + H_3 > 0$. The energy surface is given by:

$$\frac{\lambda}{2}\left(p_1^2 - q_1^2\right) + \frac{\omega_2}{2}\left(p_2^2 + q_2^2,\right) + \frac{\omega_3}{2}\left(p_3^2 + q_3^2,\right) = H_1 + H_2 + H_3 = H > 0, \quad H_1 > 0,\, H_2,\, H_3 \geq 0. \tag{28}$$

The intersection of $q_1 = 0$ with this energy surface is given by:

$$\frac{\lambda}{2}\,p_1^2 + \frac{\omega_2}{2}\left(p_2^2 + q_2^2,\right) + \frac{\omega_3}{2}\left(p_3^2 + q_3^2,\right) = H_1 + H_2 + H_3 = H > 0, \quad H_1 > 0,\, H_2,\, H_3 \geq 0. \tag{29}$$

This is the isoenergetic DS. It has the form of a 3-sphere in the six dimensional $(q_1, p_1, q_2, p_2, q_3, p_3)$ space. It has two ''halves" corresponding to the forward and backward reactions, respectively:

$$\frac{\lambda}{2}\,p_1^2 + \frac{\omega_2}{2}\left(p_2^2 + q_2^2,\right) + \frac{\omega_3}{2}\left(p_3^2 + q_3^2,\right) = H_1 + H_2 + H_3 = H > 0, \quad p_1 > 0, \quad \text{forward DS}, \tag{30}$$

$$\frac{\lambda}{2}\,p_1^2 + \frac{\omega_2}{2}\left(p_2^2 + q_2^2,\right) + \frac{\omega_3}{2}\left(p_3^2 + q_3^2,\right) = H_1 + H_2 + H_3 = H > 0, \quad p_1 < 0, \quad \text{backward DS}. \tag{31}$$

The forward and backward DS ''meet" at $p_1 = 0$:

$$\frac{\omega_2}{2}\left(p_2^2 + q_2^2,\right) + \frac{\omega_3}{2}\left(p_3^2 + q_3^2,\right) = H_2 + H_3 \geq 0, \quad \text{NHIM}, \tag{32}$$

which is a normally hyperbolic invariant 3 sphere. It is *invariant* because on this set $q_1 = p_1 = 0$ and, from (27), if $q_1 = p_1 = 0$ then $\dot{q}_1 = \dot{p}_1 = 0$. Hence, q_1 and p_1 always remain zero, and therefore trajectories with these initial conditions always remain on (32). In other words, it is invariant. It is normally hyperbolic for the same reasons as for our 2 DoF example. The directions normal to (32), i.e. $q_1 - p_1$, are linearized saddle like dynamics.

Similar to our discussion for the two degree-of-freedom index one saddle point given above, note that for $H_1 = 0$, $H_2 = 0$ and $H_3 = 0$ the NHIM reduces to the point $(q_1, p_1, q_2, p_2, q_3, p_3) = (0, 0, 0, 0, 0, 0)$, which is the index one saddle point for the full three DoF system on the energy surface $H_1 + H_2 + H_3 = 0$. Hence, as the total energy is increased from 0, with H_2 increasing from zero and/or H_3 increasing from zero, we see that the NHIM ''grows" from the index one saddle point on the zero energy surface into an invariant 3 sphere. It is in this way, as we have noted, that the ''influence" of the index one saddle point is carried to higher energies.

The stable and unstable manifolds of the NHIM are given by:

$$W^u\,(\text{NHIM}) = \left\{(q_1, p_1, q_2, p_2, q_3, p_3)\,|\,q_1 = p_1,\ \frac{\omega_2}{2}\left(p_2^2 + q_2^2\right) + \frac{\omega_3}{2}\left(p_3^2 + q_3^2\right) = H_2 + H_3 > 0\right\}, \quad (33)$$

$$W^s\,(\text{NHIM}) = \left\{(q_1, p_1, q_2, p_2, q_3, p_3)\,|q_1 = -p_1,\ \frac{\omega_2}{2}\left(p_2^2 + q_2^2\right) + \frac{\omega_3}{2}\left(p_3^2 + q_3^2\right) = H_2 + H_3 > 0\right\}. \quad (34)$$

These stable and unstable manifolds are each four dimensional on a fixed five dimensional energy surface. They have the structure of the cartesian product of a line ($q_1 = p_1$ or $q_1 = -p_1$) with a 3 sphere ($\frac{\omega_2}{2}\left(p_2^2 + q_2^2\right) + \frac{\omega_3}{2}\left(p_3^2 + q_3^2\right) = H_2 + H_3 > 0$). Mathematically, these are sometimes referred to as ''spherical cylinders". The energy of these manifolds is determined as follows. The lines ($q_1 = p_1$ or $q_1 = -p_1$) correspond to the contour $H_1 = 0$. Therefore, in the six dimensional phase space, these manifolds have energy:

$$H = H_1 + H_2 + H_3 = 0 + H_2 + H_3 > 0.$$

Using the same argument as we gave for the 1 DoF saddle and 2 DoF saddle, we choose a point $(q_1, p_1, q_2, p_2, q_3, p_3)$ on $W^u\,(\text{NHIM})$. As $t \to \infty$ the (q_2, p_2, q_3, p_3) components evolve quasiperiodically and the (q_1, p_1) grow at an exponential rate as $t \to \infty$. Similarly, if we choose a point $(q_1, p_1, q_2, p_2, q_3, p_3)$ on $W^s\,(\text{NHIM})$. As $t \to \infty$ the (q_2, p_2, q_3, p_3) components evolve quasiperiodically and the (q_1, p_1) decay to zero at an exponential rate as $t \to \infty$. In other words, trajectories starting in $W^u\,(\text{NHIM})$ decay at an exponential rate to the NHIM as $t \to -\infty$ and trajectories starting in $W^s\,(\text{NHIM})$ decay at an exponential rate to the NHIM as $t \to \infty$

2.4 Summary: NHIMs and DSs in Phase Space Associated with Index One Saddles

Here we summarize the main results above.

1 DoF: This is a ''degenerate case" in the sense that the only candidate for a NHIM, the saddle equilibrium at the origin, only exists on the $H = 0$ energy surface. On a given one dimensional energy surface the forward DS consists of a single point, which is the intersection of the energy surface with the positive p axis and the backward DS consists of the single point, which is the intersection of the energy surface with the negative p axis.

2 DoF: On a fixed three dimensional energy surface the NHIM is an unstable periodic orbit. In this 3D energy surface the DS is a 2 dimensional sphere (S^2). The 1 dimensional NHIM serves as the equator of this sphere, dividing the DS into the forward DS and the backward DS.

3 DoF: On a fixed five dimensional energy surface the NHIM is a normally hyperbolic invariant three dimensional sphere, S^3. In this 5D energy surface the DS is a 4 dimensional sphere (S^4). The 3 D NHIM serves as the equator of this 4 dimensional sphere, dividing the DS into the forward DS and the backward DS.

n DoF, n > 3: In general, on a fixed 2n-1 dimensional energy surface the NHIM is a normally hyperbolic invariant 2n-3 dimensional sphere, S^{2n-3}. In this 2n-1 dimensional energy surface the DS is a 2n-2 dimensional sphere (S^{2n-2}). The 2n-3 dimensional NHIM serves as the equator of this 2n-2 dimensional sphere, dividing the DS into the forward DS and the backward DS.

The Poincaré-Birkhoff Normal Form: The examples given above were extremely simple. In particular, each Hamiltonian was quadratic corresponding to a linear Hamiltonian vector field. Therefore there is a question as to whether or not ''similar calculations" can be carried out for more general Hamilton's equations? The answer is ''yes", and the analytical and computational tool that facilitates this is the Poincaré-Birkhoff normal form. In a neigborhood of an index k saddle point, this technique provides a coordinate system in which the Hamiltonian can be accurately approximated by an *integrable* Hamiltonian system. For index 1 saddles this integrable structure allows us to explicitly construct NHIMs and DSs (as well as other phase space structures) analogous to those described in the above examples (and with the same properties, e.g. the NHIM is the equator of a DS having the ''no-recrossing" property). The normal form algorithm also provides a symplectic transformation that allows us to map the phase space surfaces back into the original ''physical coordinates". A general description of this technique, relevant to both classical and quantum reaction dynamics, can be found in Waalkens *et al.* (2008).

NHIMs vs. saddles: Saddle points (i.e. equilibrium points of Hamilton's equations of saddle stability type) can only exist on a fixed energy surface. NHIMs, on the other hand, exist for a range of energies above the energy of the saddle point. The NHIM is a ''dynamical object" in the sense that it is composed of trajectories. Therefore the NHIM ''carries" the saddle point behavior to a range of energies. If we view the energy as a ''bifurcation parameter", NHIMs bifurcate from saddle points as the energy is increased from that of the saddle.

''No-recrossing" of the DS: We want to explicitly point out some of the key features of the ''no-recrossing" property of the DS. Our Hamiltonians were all expressed in terms of a set of coordinates:

$$(q_1, p_1, q_2, p_2, \ldots, q_n, p_n),$$

where (q_1, p_1) described saddle point (i.e. ''hyperbolic") behavior and the remaining coordinates described oscillator (i.e. ''elliptic") behavior. In general, this type of dynamics is realized through the Poincaré-Birkhoff normalization technique, but we chose examples illustrating behavior in order to focus on particular issues that avoid the risk of being obscured with computational complexities.

Now in all cases, regardless of the DoF, in these coordinates reaction means a change in the sign of the q_1 coordinate. Thus, it was natural to obtain a dividing surface by setting $q_1 = 0$, which gave a surface in phase space when setting $q_1 = 0$ in the Hamiltonian–a surface with two ''halves" separated by the NHIM (i.e. the NHIM is the equator for the surface, that has the structure of a sphere).What ''no-recrossing" means is that the Hamiltonian vector field is never zero or tangent to the DS at any point on the DS. Now, from Hamilton's equations we have $\dot{q}_1 = p_1$ and, by construction, p_1 is positive on the forward DS and negative on the backward DS. Therefore trajectories starting on the respective DS leave the DS in the same direction. When $p_1 = 0$ and $q_1 = 0$ these correspond to trajectories starting on the *invariant* NHIM.

We also point out that the no-recrossing property is stable under perturbation. This means stable under perturbation to the Hamiltonian vector field or to the equation for the DS (which is related to the Hamiltonian vector field since the DS is obtained via a constraint ($q_1 = 0$) on the Hamiltonian. This can be seen as follows. no-recrossing means that the vector field is transverse to the DS everywhere (except, of course, at the NHIM). This means that at any point on the DS, the angle between the velocity vector and the tangent vector to the DS (at that point) is bounded away from zero, Clearly, this is a property that is ''stable under perturbations".

Persistence under perturbation: A fundamental property of NHIMs that is extremely useful for applications is that NHIMs ''persist under perturbations". Another way of saying this is that they are ''stable under perturbation". This property is proven in all of the basic mathematical references concerning NHIMs that we noted in the introduction. But what does it mean? NHIMs can cease to exist when

they are no longer normally hyperbolic. Now note that NHIMs are functions of energy. It may happen that normally hyperbolicity is lost as the energy is varied. Like ''loss of hyperbolicity" in general for dynamical systems, this can lead to ''bifurcation of NHIMs". This phenomenon has been studied in Li *et al.* (2009); Inarrea *et al.* (2011); Allahem and Bartsch (2012); Mauguière *et al.* (2013); MacKay and Strub (2014); MacKay and Strub (2015).

3 A ''Global" Dividing Surface

The influence of index two saddle points on reaction dynamics has been studied in Ezra and Wiggins (2009a); Collins *et al.* (2011); Haller *et al.* (2010); Mauguiere *et al.* (2013). The construction of a dividing surface for general index k saddles was given in Collins *et al.* (2011). However, in this section we describe a ''global dividing surface" that is associated with an index two saddle point and two index one saddle points. Such a structure was constructed in analyzing the isomerization dynamics of a buckled nanobeam in Collins *et al.* (2012). Intriguingly, a similar geometrical structure arose on the study of the so-called "roaming phenomenon" in Harding *et al.* (2012); Suits and Parker (2014). Consequently, this type of geometrical structure could be more widespread in reaction dynamics so we believe it may be useful to give an analytically tractable example of such a situation.

As opposed to our linear examples above, for the system to have multiple saddle points it must be nonlinear. We will consider two identical uncoupled two well potential systems, as shown in Fig. 4.

The Hamiltonian for this system is given by:

$$H = \underbrace{\frac{p_1^2}{2} - \frac{q_1^2}{2} + \frac{q_1^4}{4}}_{H_1} + \underbrace{\frac{p_2^2}{2} - \frac{q_2^2}{2} + \frac{q_2^4}{4}}_{H_2}, \tag{35}$$

with the associated Hamiltonian vector field:

$$\begin{aligned}
\dot{q}_1 &= \frac{\partial H}{\partial p_1} = p_1, \\
\dot{p}_1 &= -\frac{\partial H}{\partial q_1} = q_1 - q_1^3, \\
\dot{q}_2 &= \frac{\partial H}{\partial p_2} = p_2, \\
\dot{p}_2 &= -\frac{\partial H}{\partial q_2} = q_2 - q_2^3.
\end{aligned} \tag{36}$$

The potential energy is given by:

$$V(q_1, q_2) = -\frac{q_1^2}{2} + \frac{q_1^4}{4} - \frac{q_2^2}{2} + \frac{q_2^4}{4}. \tag{37}$$

The potential energy has nine critical points, which we list below, along with their stability type and total energy:

$$\begin{array}{rll}
(0,0), & \text{index two saddle,} & \text{total energy } 0, \\
(0,1),(0,-1),(1,0),(-1,0), & \text{index one saddles,} & \text{total energy } -1/4, \\
(1,1),(1,-1),(-1,1),(-1,-1), & \text{minima,} & \text{total energy } -1/2,
\end{array} \tag{38}$$

We illustrate the critical points of (37) in Fig. 5.

In order to consider a surface to be a dividing surface we need to understand what the surface is dividing. In the language of chemical reactions, index one saddles give rise to dividing surfaces that divide reactants and products. The examples above were designed only to illustrate the geometry associated with the passage of trajectories through a dividing surface. In particular, in the examples "reactants" corresponded to a region have a particular sign of the q_1 coordinate and ''products" corresponded to a region corresponding to the

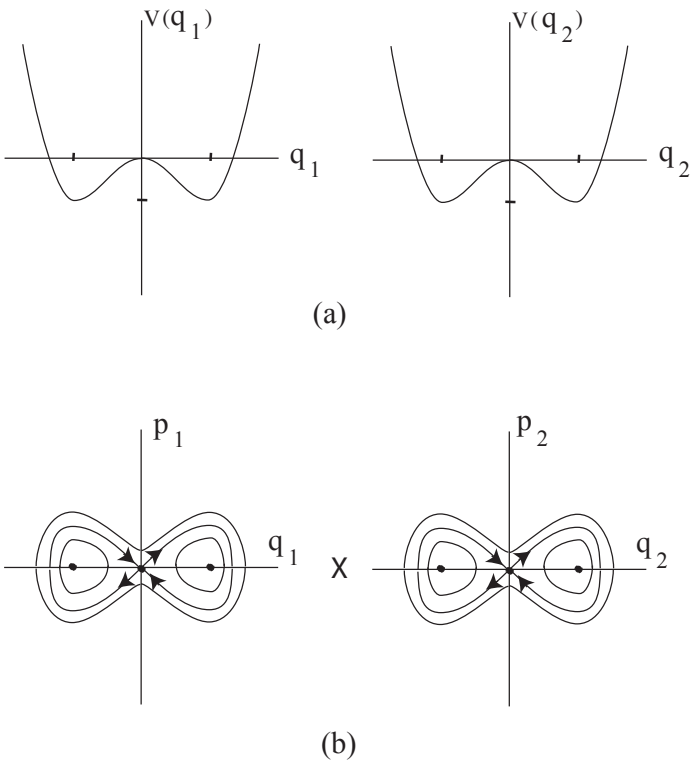

Figure 4: a) Graphs of the potential energy for the two uncoupled two well systems. b) Phase portraits for the two uncoupled two well systems.

opposite sign of the q_1 coordinate. and it was arbitrary which region was considered reactants and which products.

For this example there are multiple wells, index one saddles, and one index two saddle. A natural question to consider is how do the saddles influence the motion of trajectories between the different wells? To some extent this question has been analyzed in Collins *et al.* (2011). However, here our goal will be only to construct a dividing surface that incorporates the index two saddle and two index one saddles, and to describe the role that these three saddles play in the dividing surface. Towards this end we consider the ''reaction problem" of trajectories crossing $q_2 = 0$, but from a phase space perspective.

The three dimensional energy surface is given by:

$$\frac{p_1^2}{2} - \frac{q_1^2}{2} + \frac{q_1^4}{4} + \frac{p_2^2}{2} - \frac{q_2^2}{2} + \frac{q_2^4}{4} = H_1 + H_2 = H, \tag{39}$$

and a two dimensional DS separating trajectories with $q_2 < 0$ from trajectories with $q_2 > 0$ is given by:

$$\frac{p_1^2}{2} - \frac{q_1^2}{2} + \frac{q_1^4}{4} + \frac{p_2^2}{2} = H_1 + H_2 = H. \tag{40}$$

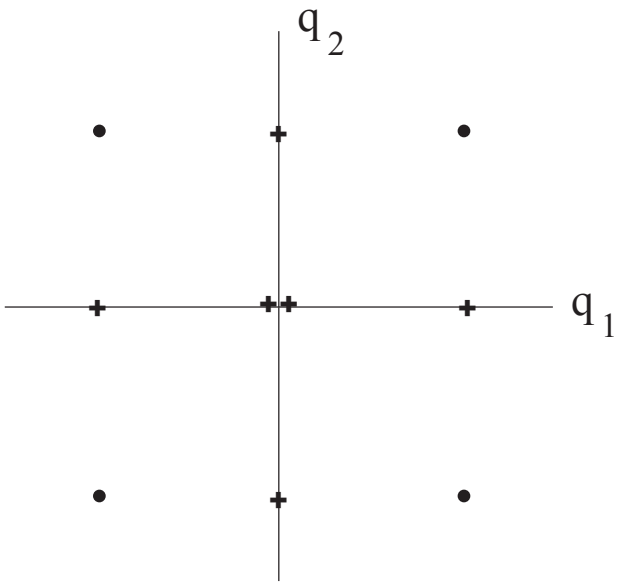

Figure 5: Critical points of (37). ++ denotes the index two saddle, + denotes index one saddles, and the black circles denote the minima.

The value of the total energy, H, plays a very important role in whether or not trajectories can cross this DS, as well as *how* they cross this DS.

Suppose we take:

$$-1/4 < H_2 < 0, \quad H_1 > 0.$$

In this case the q_2 component on a trajectory cannot change sign, but the q_1 component can change sign. This corresponds to crossing $q_2 = 0$ by passing through one of the dividing surfaces corresponding to one of the index one saddles. As H_2 increases through zero, these two DSs merge, and now both the q_1 and the q_2 components of trajectories can change sign. In this way the index two saddle can be ''crossed". A symbolic description of the different types of trajectories classified in terms of how they cross $q_2 = 0$ and their relation to the different saddles during the crossing is given in Ezra and Wiggins (2009a); Collins *et al.* (2011).

Finally, it is instructive to consider the word ''global" in the phrase ''global dividing surface". In this example there are two wells with $q_2 > 0$ and two wells with $q_2 < 0$. If one considers a reactive trajectory to be one that evolves from one well to another, typically one considers a dividing surface that only separates two wells. In this sense it is a ''local dividing surface". However, in this example the dividing surface is a

boundary with multiple wells on each side of $q_2 = 0$. In order to give this configuration of wells, saddles, and global dividing surface meaning in a chemical reaction context, specific examples must be considered. In this regard, the examples concerning with "roaming reactions" (see, e.g. Bowman and Suits (2011); Bowman and Shepler (2011)) discussed in Shepler *et al.* (2011); Harding *et al.* (2012) are particularly interesting. They consider a global dividing surface that has the essential features of our example in that it is constructed from two index one saddles and an index two saddle at a higher energy than the index two.

4 Summary and Outlook

In this paper we have described how the notion of a normally hyperbolic invariant manifold (NHIM) is used in chemical rection dynamics. We have done this by considering simple examples for one, two, and three degree-of-freedom systems where explict calculations could be carried out for all of the relevant geometrical stuctures and their properties could be explicitly understood. We specifically emphasised the notion of a NHIM as a "phase space concept". In particular, we made the observation that the (phase space) NHIM played the role of "carrying" the (configuration space) properties of a saddle point into phase space.

Finally, we considered an explicit example of a 2 degree-of-freedom system where a "global" dividing surface could be constructed using two index one saddles and one index two saddle. Such a dividing surface has arisen in several recent applications and, therefore, such a construction could be of wider interest and certaily deserves further studies.

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References

Allahem, A. and Bartsch, T. (2012). Chaotic dynamics in multidimensional transition states. *J. Chem. Phys.*, **137**, 214310.

Bowman, J. M. and Shepler, B. C. (2011). Roaming radicals. *Ann. Rev. Phys. Chem.*, **62**, 531–553.

Bowman, J. M. and Suits, A. G. (2011). Roaming reaction: The third way. *Phys. Today*, **64**(11), 33.

Bunker, D. L. and Hase, W. L. (1973). On non-RRKM unimolecular kinetics: Molecules in general, and CHNC in particular. *The Journal of Chemical Physics*, **59**, 4621.

Carpenter, B. (1998). Dynamic behavior of organic reactive intermediates. *Angew. Chimie (Intl Ed.)*, **37**, 3341–3350.

Carpenter, B. K. (2003a). Nonexponential decay of reactive intermediates: new challenges for spectroscopic observation, kinetic modeling and mechanistic interpretation. *J. Phys. Org. Chem.*, **16**, 858–868.

Carpenter, B. K. (2003b). Nonexponential decay of reactive intermediates: new challenges for spectroscopic observation, kinetic modeling and mechanistic interpretation. *Journal of physical organic chemistry*, **16**(11), 858–868.

Carpenter, B. K. (2005). Nonstatistical dynamics of thermal reactions of polyatomic molecules. *Ann. Rev. Phys. Chem.*, **56**, 57–89.

Child, M. S. and Pollak, E. (1980). Analytical reaction dynamics:Origin and implications of trapped periodic orbits. *J. Chem. Phys.*, **73**(9), 4365–4372.

Collins, P., Ezra, G. S., and Wiggins, S. (2011). Index k saddles and dividing surfaces in phase space with applications to isomerization dynamics. *The Journal of Chemical Physics*, **134**(24), 244105.

Collins, P., Ezra, G. S., and Wiggins, S. (2012). Isomerization dynamics of a buckled nanobeam. *Phys. Rev. E*, **86**, 056218.

Ezra, G. and Wiggins, S. (2009a). Phase-space geometry and reaction dynamics near index 2 saddles. *Journal of Physics A: Mathematical and Theoretical*, **42**(20), 205101.

Ezra, G. S. and Wiggins, S. (2009b). Impenetrable barriers in phase space for deterministic thermostats. *Journal of Physics A: Mathematical and Theoretical*, **42**(4), 042001.

Fenichel, N. (1971). Persistence and smoothness of invariant manifolds for flows. *Indiana Univ. Math. J*, **21**(193-226), 1972.

Fenichel, N. (1974). Asymptotic stability with rate conditions. *Indiana Univ. Math. J.*, **23**, 1109–1137.

Fenichel, N. (1977). Asymptotic stability with rate conditions, ii. *Indiana Univ. Math. J.*, **26**, 81–93.

Gillilan, R. E. and Ezra, G. S. (1991). Transport and turnstiles in multidimensional Hamiltonian mappings for unimolecular fragmentation: Application to van der Waals predissociation. *J. Chem. Phys.*, **94**, 2648–2668.

Glowacki, D., Stephen, S. M., and Pilling, M. (2009). Significance of Nonstatistical Dynamics in Organic Reaction Mechanisms: Time-Dependent Stereoselectivity in Cyclopentyne-Alkene Cycloadditions. *JACS*, **131**, 13896–13897.

Goldman, L., Glowacki, D., and Carpenter, B. (2011). Nonstatistical Dynamics in Unlikely Places: [1,5] Hydrogen Migration in Chemically Activated Cyclopentadiene. *JACS*, **133**, 5312–5318.

Haller, G., Palacian, J., Yanguas, P., Uzer, T., and Jaffé, C. (2010). Transition States Near Rank-Two Saddles: Correlated Electron Dynamics of Helium. *Comm. Nonlinear Sci. Num. Simul.*, **15**, 48–59.

Harding, L. B., Klippenstein, S. J., and Jasper, A. W. (2012). Separability of Tight and Roaming Pathways to Molecular Decomposition. *J. Phys. Chem. A*, **116**, 6967–6982.

Hirsch, M. W., Pugh, C. C., and Shub, M. (1977). *Invariant manifolds*, volume 583 of *Lecture Notes in Mathematics*. Springer-Verlag, New York, Heidelberg, Berlin.

Inarrea, M., Palacian, J. F., Pascual, A. I., and Salas, J. P. (2011). Bifurcations of dividing surfaces in chemical reactions. *J. Chem. Phys.*, **135**, 014110.

Li, C.-B., Toda, M., and Komatsuzaki, T. (2009). Bifurcation of no-return transition states in many-body chemical reactions. *J. Chem. Phys.*, **130**(12), 124116.

MacKay, R. S. and Strub, D. C. (2014). Bifurcations of transition states: Morse bifurcations. *Nonlinearity*, **27**(5), 859.

MacKay, R. S. and Strub, D. C. (2015). Morse bifurcations of transition states in bimolecular reactions. *Nonlinearity*, **28**(12), 4303–4329.

Mauguiere, F., Collins, P., Ezra, G., and Wiggins, S. (2013). Bond breaking in a Morse chain under tension: Fragmentation patterns, higher index saddles, and bond healing. *J. Chem. Phys.*, **138**, 134118.

Mauguière, F. A. L., Collins, P., Ezra, G. S., and Wiggins, S. (2013). Bifurcations of normally hyperbolic invariant manifolds in analytically tractable models and consequences for reaction dynamics. *Int. J. Bifurcat. Chaos*, **23**(12).

Pechukas, P. and Pollak, E. (1979). Classical transition state theory is exact if the transition state is unique. *The Journal of Chemical Physics*, **71**, 2062.

Pollak, E., Child, M. S., and Pechukas, P. (1980). Classical transition state theory: a lower bound to the reaction probability. *J. Chem. Phys.*, **72**, 1669–1678.

Rehbein, J. and Carpenter, B. (2011). Do we Fully Understand what Controls Chemical Selectivity. *PCCP*, **13**, 20906–20922.

Shepler, B. C., Braams, B. J., and Bowman, J. M. (2008). "Roaming" dynamics in CH_3CHO photodissociation revealed on a global potential energy surface. *J. Phys. Chem. A*, **112**, 9344–9351.

Shepler, B. C., Han, Y., and Bowman, J. M. (2011). Are Roaming and Conventional Saddle Points for H_2CO and CH_3CHO Dissociation to Molecular Products Isolated From Each Other? *J. Phys. Chem. Lett.*, **2**(7), 834–838.

Suits, A. G. and Parker, D. H. (2014). Hot molecules: Off the beaten path. *Science*, **346**, 30–31.

Waalkens, H. and Wiggins, S. (2004). Direct construction of a dividing surface of minimal flux for multi-degree-of-freedom systems that cannot be recrossed. *J. Phys. A: Math. Gen.*, **37**(35), L435.

Waalkens, H. and Wiggins, S. (2010). Geometrical models of the phase space structures governing reaction dynamics. *Regular and Chaotic dynamics*, **15**(1), 1–39.

Waalkens, H., Schubert, R., and Wiggins, S. (2008). Wigner's dynamical transition state theory in phase space: classical and quantum. *Nonlinearity*, **21**, R1–R118.

Wiggins, S. (1990). On the geometry of transport in phase space I. Transport in k degree-of-freedom Hamiltonian systems, $2 \leq k < \infty$. *Physica D*, **44**, 471–501.

Wiggins, S. (1994). *Normally hyperbolic invariant manifolds in dynamical systems*, volume 105. Springer.

Wigner, E. (1938). The transition state method. *Trans. Faraday Soc.*, **34**, 29–41.

Zheng, J., Papajak, E., and Truhlar, D. (2009). Phase Space Prediction of Product Branching Ratios: Canonical Competitive Nonstatistical Model. *JACS*, **131**, 15754–15760.